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Effects of Nb doping on highly fatigue-resistant thin films of $(Pb_{0.8}Ba_{0.2})ZrO_3$ for ferroelectric memory application

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Abstract

Niobium-doped $(Pb_{0.8}Ba_{0.2})ZrO_3$ (PBNZ) thin films were prepared by RF-magnetron sputtering at room temperature followed by postannealing at 700 °C. The doping concentration of Nb is in the range from 0 up to 2.5 at%. The introduction of Nb enhances the ferroelectric property and suppresses the leakage current of the PBNZ films. A large remanent polarization (P_r) of $2P_r = 35\,\mu C/cm^2$ can be obtained from a doping of 1.5 at% Nb in the PBNZ film in comparison to that of $19\,\mu C/cm^2$ from the undoped PBZ film. The Pt/PBNZ/Pt capacitor also exhibits a high fatigue resistance against polarization switching up to 10^{10} cycle as that of Pt/PBZ/Pt. Moreover, an improvement of retention property can be also achieved from Nb doping.
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1. Introduction

Ferroelectric thin films have attracted a great attention for application in nonvolatile semiconductor memories, i.e. ferroelectric random access memory (FeRAM), because of their many advantages over Si-based devices [1–3]. Among the many materials, $Pb(Zr_xTi_{1-x})O_3$ (PZT) is mostly investigated for the above application due to its superior properties of high remanent polarization and low operation voltage [4,5]. Unfortunately, the PZT contains a high content of oxygen vacancies, which are easy to entrap at the ferroelectric/electrode interface during polarization reversals and degrade the polarization ability when metal electrode is used [6]. In order to improve the

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fatigue problem, the layered-perovskite films, such as $SrBi_2Ta_2O_9$ (SBT) [7] or $Bi_{4-x}La_xTi_3O_{12}$ (BLT) [8], were developed, which have a high fatigue resistance against polarization switching. However, the layered-perovskites usually have a low remanent polarization (P_r), e.g. $2P_r = 4$–$16\,\mu C/cm^2$ for SBT and 16–20 $\mu C/cm^2$ for BLT, as compared to that, 20–70 $\mu C/cm^2$, for PZT. The $(Pb_{1-x}Ba_x)ZrO_3$ (PBZ) with $x = 0.2-0.4$ is another ferroelectric material having a simple perovskite structure as that of PZT. It is a solid solution of the antiferroelectric $PbZrO_3$ (PZO) and paraelectric $BaZrO_3$ (BZO) [9]. The ferroelectric PBZ film also has a high fatigue resistance against polarization switching because it contains less oxygen vacancies than PZT due to the exclusion of Ti in the films [10]. Nevertheless, the thin films have a relatively low remanent polarization and high leakage current which are disadvantageous for application. It is well known that the properties of ferroelectric materials can be modified by the addition of dopants, in particular, the donor dopants such as Nb [11,12]. In general, the donor dopants increase the electrical resistance and enhance the remanent polarization of the ferroelectric materials. Therefore, the effect of Nb doping on the properties of PBZ films with a composition near the morphotropic phase boundary is investigated.

2. Experimental details

The PBZ and Nb-doped PBZ (PBNZ) films of 150 nm thickness were prepared by co-sputtering of the $(Pb_{0.8}Ba_{0.2})ZrO_3$ and $(Pb_{0.8}Ba_{0.2})(Nb_{0.1}Zr_{0.9})O_3$ ceramic targets, in which 10% excess PbO was added to compensate the Pb loss during thermal process. The films were deposited on Pt (150 nm)/TiN (75 nm)/Ti (40 nm)/SiO_2 (200 nm)/Si substrate by RF magnetron sputtering. No heating of the substrate was done during the sputtering and the deposited films were then crystallized by rapid thermal annealing at 700 °C for 3 min in O_2 ambient. The PBNZ films have a chemical composition of $(Pb_{0.8}Ba_{0.2})(Nb_xZr_{1-x})O_3$ with $x = 0-0.025$, as determined from inductively coupled plasma spectrometry (ICP) with an accuracy of ± 3 at%, and the X-ray diffraction confirms all the films are well crystallized into a psuedocubic phase of perovskite with a random orientation. To measure the electrical properties, Pt top electrode was deposited onto the PBNZ films.

3. Results and discussion

The dielectric property of the PBNZ films was first investigated with impedance analyzer. Fig. 1 shows the change of dielectric constant and loss ($\tan\delta$) as a function of Nb doping content. The dielectric constant increases with increasing the Nb content, from a value of 260 to 600 for a doping of 2.5 at% Nb. According to perovskite defect chemistry, the charge compensation of donor dopant would suppress the generation of oxygen vacancies. As the oxygen vacancies are easy to entrap at the grain boundaries, domain walls or interfaces, which would retard the movement of domain wall [13], the dielectric response is thus enhanced by the addition of Nb in the PBNZ films. The leakage current characteristic of the PBNZ films was then measured at room temperature. Fig. 2 displays the measured current density of PBNZ films as a function of applied field. In association with the reduction of oxygen vacancies, the leakage current is suppressed and the breakdown field is raised with increasing the Nb content in the

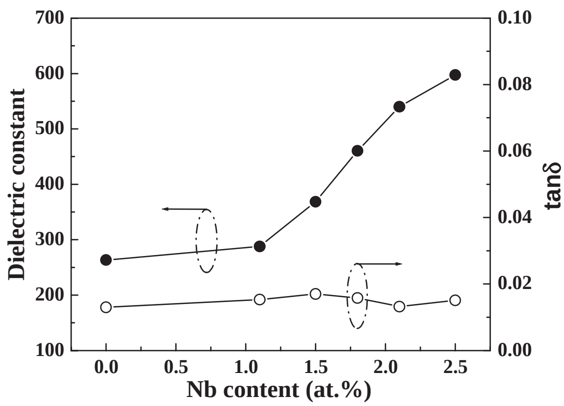

Fig. 1. Change of the dielectric constant and dielectric loss with increasing the Nb concentration in the PBNZ films.

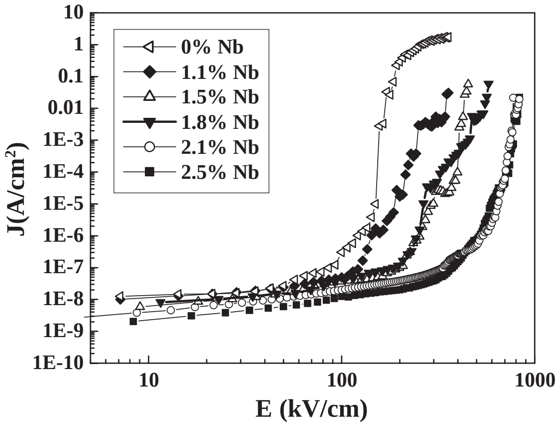

Fig. 2. Current density (J) versus applied electric field (E) of the PBNZ films.

PBZ films which is in good agreement with the results of Nb-doped PZT films [14–16].

The polarization–electric field (P-E) hysteresis loops of PBNZ films with the different Nb-doping concentrations, measured using TF2000 (aix-ACCT Systems, GmbH) at room temperature in the capacitor configuration of Pt/PBNZ/Pt, are depicted in Fig. 3(a). As shown in Fig. 3(b), with an increase of Nb content from 0 to 1.5 at%, the remanent polarization ($2P_r$) largely increases from 19 to 35 $\mu C/cm^2$ and decreases with further increase of doping, but the coercive field ($2E_c$) only slightly changes from 246 to 270 kV/cm. The result can be understood from the type of vacancy formed when donors are incorporated into the PBZ lattice. In addition to the suppression of mobile oxygen vacancies, the compensation of excess positive charges from donors could also induce the generation of A-site, i.e. Pb-site, vacancies in the films. The former would reduce the pinning of domain wall and the later is helpful to minimize the local constraint stress against polarization reversal [17]. Therefore, an enhancement of P_r value can be obtained. However, a reduction of ferroelectricity could result due to the loss of tetragonality of the perovskite lattice when too much dopant is added into the PBZ films [14], and cause the decrease of P_r value for Nb doping over 1.5 at%.

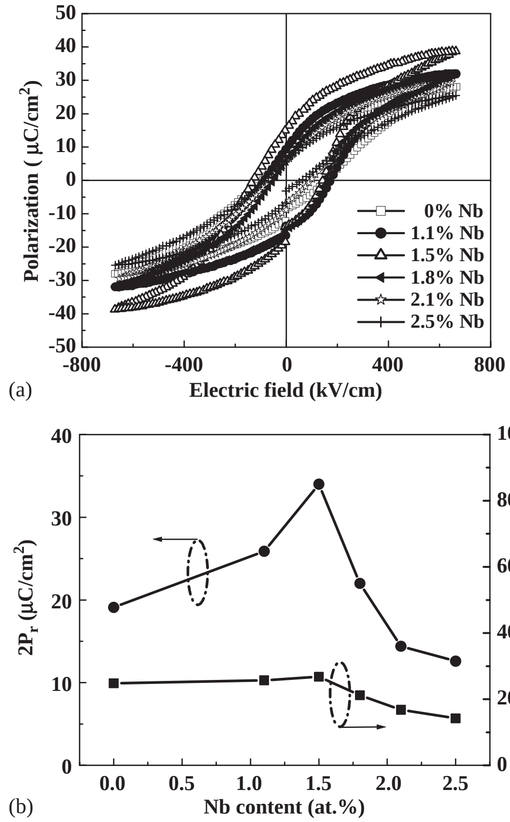

Fig. 3. (a) Polarization–electric filed hysteresis loops of the PBNZ thin films, and (b) the change of the remanent polarization, $2P_r$, and coercive filed, $2E_c$, as a function of the Nb content.

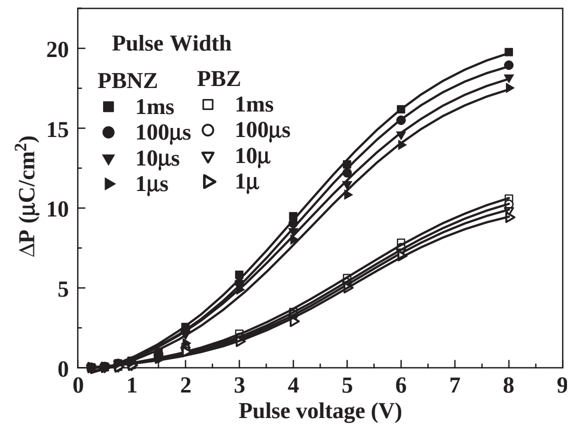

Fig. 4. Pulse polarization, ΔP, versus pulse voltage measured with different pulses width, for the PBZ and PBNZ (1.5 at%) films.

The pulsed polarization (ΔP) measurement of the PBZ and PBNZ (1.5 at%) films further confirms the enhancement of ferroelectric property, as illustrated in Fig. 4. The PBNZ films has a ΔP value two times larger than that of the PBZ film irrespective of the pulse voltage, and the polarization value only slightly decreases with decreasing the pulse width for both films. The change in net polarization, $2P_r$, of the above two films as a function of switching cycles was then tested with bipolar pulse trains of ± 6 V (± 400 kV/cm) using a 1 MHz square wave signal. The result is shown in Fig. 5. A high endurance of polarization switching up to 10^{10} cycles can be obtained for both films. Thus, the property of high fatigue resistance is preserved in the Nb-doped PBZ film, although it has an enhanced polarization of switching. Another advantage of Nb doping is the improvement in the retention characteristic, as shown in Fig. 6. The retention tests were carried out at 6 V with a write pulse width of 5 ms and a read pulse width of 2 ms. The switched polarization (ΔP) of PBNZ (1.5 at%) film decreases from 14.6 to 11.9 $\mu C/cm^2$, i.e. about 20% drop of polarization value, for a retention from 1 to 10^4 s, but, the ΔP value of PBZ film decreases by about 32%, from 6.0 to 4.1 $\mu C/cm^2$, for the same retention. The improvement in the retention property may also correlate to the minimization of local stress against polarization reversal by the generation of A-site vacancies from Nb doping.

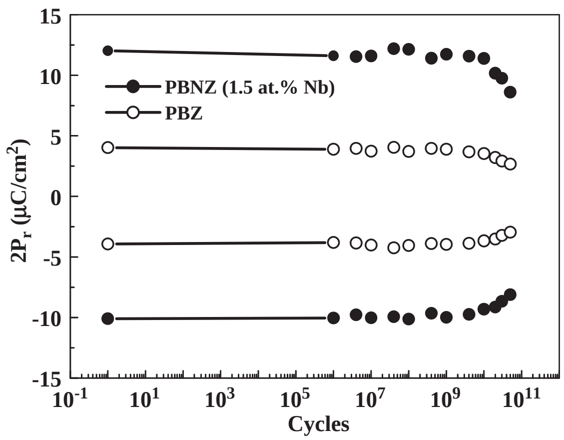

Fig. 5. Polarization fatigue behaviors of Pt/PBZ/Pt and Pt/PBNZ (1.5 at%)/ Pt capacitors measured with bipolar pulsed pulse trains of ± 6 V.

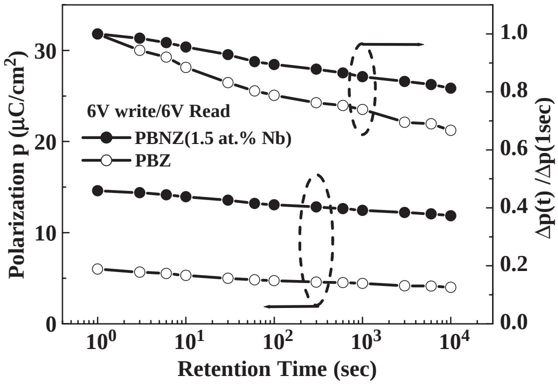

Fig. 6. Switched polarization, ΔP, as a function of retention time for the Pt/PBZ/Pt and Pt/PBNZ (1.5 at%)/Pt capacitors.

4. Conclusions

From this study, it is clear that the Nb-doped PBZ films have the characteristics of large remanent polarization, low leakage current, high fatigue resistance, and improved retention property, which are comparable or superior to those of layered-perovskite films, such as SBT or BLT. Since the simple perovskite oxide is usually easy to fabricate comparing to the layered-perovskite oxides, the PBNZ films are promising to replace the conventional high-fatigue-resistance thin films of SBT or BLT for application in FeRAMs.

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